

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
26 September 2002 (26.09.2002)

PCT

(10) International Publication Number
WO 02/074891 A2

(51) International Patent Classification⁷: **C11D 17/04**,
3/39, 3/395

(21) International Application Number: **PCT/EP02/02770**

(22) International Filing Date: **11 March 2002 (11.03.2002)**

(25) Filing Language: **English**

(26) Publication Language: **English**

(30) Priority Data:
09/810,106 16 March 2001 (16.03.2001) **US**

(71) Applicant (for *AE, AG, AU, BB, BZ, CA, CY, GB, GD, GH, GM, IE, IL, KE, LC, LK, LS, MN, MW, NZ, OM, SD, SG, SL, SZ, TT, TZ, UG, ZA, ZM, ZW* only): **UNILEVER PLC** [GB/GB]; Unilever House, Blackfriars, London EC4P 4BQ (GB).

(71) Applicant (for *AL, AM, AT, AZ, BA, BE, BG, BR, BY, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, FR, GE, GR, HR, HU, ID, IS, IT, JP, KG, KP, KR, KZ, LR, LT, LU, LV, MA, MC, MD, MG, MK, MX, MZ, NL, NO, PH, PL, PT, RO, RU, SE, SI, SK, TJ, TM, TN, TR, UA, UZ, VN, YU* only): **UNILEVER NV** [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).

(71) Applicant (for *IN* only): **HINDUSTAN LEVER LIMITED** [IN/IN]; Hindustan Lever House, 165/166 Backbay Reclamation, Maharashtra, Mumbai 400 020 (IN).

(72) Inventors: **PFEIFFER, Natasha**; 235 West 100th Street, Apartment 2F, New York, NY 10025 (US). **GHATLIA,**

Naresh, Dhirajlal; LFEDC Vlaardingen, Olivier van Nootlaan 120, NL-3133 AT Vlaardingen (NL). **SECEM-SKI, Isaac, Israel**; Unilever Research U.S. Inc., 45 River Road, Edgewater, NJ 07020 (US).

(74) Agents: **MULDER, Cornelis, Willem, Reinier et al.**; Unilever PLC; Patent Department, Colworth House, Sharnbrook, Bedford, Bedfordshire MK44 1LQ (GB).

(81) Designated States (*national*): **AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZM, ZW.**

(84) Designated States (*regional*): **ARIPO** patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), **Eurasian** patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), **European** patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), **OAPI** patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *without international search report and to be republished upon receipt of that report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: **WATER SOLUBLE SACHET WITH A DISHWASHER COMPOSITION**

(57) Abstract: This invention is directed to a water soluble sachet comprising a detergent composition having an encapsulated bleach. The water soluble sachet unexpectedly results in excellent cleaning properties and minimizes spot and film formation on items being cleaned in a dishwasher.

WO 02/074891 A2

- 1 -

WATER SOLUBLE SACHET WITH A
DISHWASHER COMPOSITION

5 This invention is directed to a composition for use in a dishwashing machine. More particularly, the invention is directed to a water soluble sachet comprising such a composition along with an encapsulated bleach. The composition preferably is a gel that comprises a polymer
10 comprising a positive charge and at least one of a water soluble polymer that reduces phosphate scale formation, and a compound that reduces carbonate scale formation. The sachet unexpectedly results in excellent cleaning properties and excellent glass appearance without leaving a detergent
15 residue which is typically characteristic of dishwashing compositions in tablet or powder form.

Dishwashing compositions constitute a generally recognized distinct class of detergent compositions, particularly when
20 compared to detergents designed for fabric washing. For example, the ultimate dishwashing composition results in a spotless and film-free appearance on glassware and silverware after a cleaning cycle in a dishwashing machine. In fabric washing operations, on the other hand, detergent
25 compositions which result in greasy, oily or soapy residues on items that were cleaned can be tolerated.

Often, washing articles in a commercially available dishwashing machine entails using three products. Salt is
30 added to the salt compartment to recharge the ion exchanger which softens the water, a dishwashing formulation is used to clean the articles, and a rinse aid is used to ensure

- 2 -

that the articles are rinsed with no streaks or smears. Consumers generally find it very inconvenient, however, to replace or refill such products.

5 In order to provide convenient products to consumers, manufacturers have been making dishwashing tablets in order to eliminate detergent handling and dosing issues. Such tablets often have a detergent portion, and a wax portion which contains a rinse aid. These types of tablets, which
10 are sometimes referred to as 2-in-1 tablets, have disadvantages since they may only be used in a wash cycle that does not exceed 55°C. This is true because the wax portion which contains the rinse aid will completely dissolve in a wash cycle that exceeds 55°C. This causes all
15 of the rinse aid to drain out of the dishwashing machine before the actual rinse cycle.

Furthermore, such 2-in-1 tablets require that salt be added to the dishwashing machine in order to obtain optimal
20 results, and they are very complicated and expensive to produce.

Other types of tablets that are well known are often referred to as pH sensitive 2-in-1 tablets. These types of
25 tablets have a detergent portion and rinse aid portion that is contained in a pH sensitive material; the rinse aid portion to be released under the lower pH conditions of the rinse cycle. The pH sensitive 2-in-1 tablets may be used in wash cycles that exceed 55°C, but they are known to
30 prematurely release rinse aid in hot washes that run long. Also, like the detergent tablets with the wax portion, the

- 3 -

pH sensitive 2-in-1 tablets require that salt be added to the dishwashing machine in order to obtain optimal cleaning results and they are extremely expensive to produce.

- 5 In addition to the above-described deficiencies of conventional tablets, such conventional tablets also are known to characteristically leave residue on dishware being cleaned because they do not always completely dissolve within a dishwashing cycle. Conventional tablets are also
- 10 difficult to handle because they often require unwrapping before use. Also, those that are not wrapped can be unpleasant to handle because of fines on the surface of the tablet.
- 15 It is of increasing interest to provide a dishwashing composition that works well at all wash temperatures of a dishwashing system (even temperatures greater than 55°C), provides anti-scaling benefits in a system that is high in phosphate and/or carbonate content (in hard water), does
- 20 result in excellent cleaning benefits in water that has not been subjected to conventional water softening additives (i.e., hard water), provides a shiny glassware appearance in the absence of conventional rinse aid compositions and does not leave residue on dishware being cleaned.
- 25 This invention, therefore, is directed to a dishwashing composition that is associated with an encapsulated bleach, and preferably has a polymer comprising a positive charge and at least one of a water soluble polymer that reduces
- 30 phosphate scale formation, and a compound that reduces carbonate scale formation on glassware being cleaned. The

- 4 -

dishwashing composition is superior in that it unexpectedly results in excellent cleaning properties and reduced spotting and scale formation when no salt is added to the dishwashing machine to soften hard water, when washing
5 cycles exceed a temperature of 55°C, and when no rinse aid composition is added to the dishwashing machine. In fact, the present invention is directed to a superior 3-in-1 detergent composition that is contained in a stable water soluble sachet. Such a superior detergent composition
10 unexpectedly results in a reduction in film and spot formation even when compared to similar compositions in solid (e.g., powder/tablet) form.

Efforts have been made to prepare dishwashing compositions.
15 In U.S. Patent No. 5,939,373, an automatic dishwashing detergent composition comprising a phosphate builder and a metal containing bleach catalyst is described.

Still other efforts have been disclosed for making
20 dishwashing compositions. In WO 00/06688, a dishwashing composition with a coated core is described. The coated core has a substance that exerts its function in a clear rinse cycle.

25 Even further, other efforts have been disclosed for making dishwashing compositions. In DE 197 27 073 A1, coated detergent components are described.

None of the material above describes a dishwashing
30 composition within a water-soluble sachet wherein the dishwashing composition is in the form of a gel, and

- 5 -

comprises an encapsulated bleach. Moreover, none of the material above describes a dishwashing composition within a water soluble sachet comprising a polymer with a positive charge and a water soluble polymer that reduces phosphate
5 scale formation and/or a compound that reduces carbonate scale formation wherein the dishwashing composition results in excellent cleaning properties and glass appearance when used, for example, in the presence of hard water, in the absence of rinse aid compositions and in a washing cycle
10 that exceeds a temperature of 55°C.

In a first embodiment, the present invention is directed to a water-soluble sachet comprising a dishwashing composition wherein the dishwashing composition is a gel which comprises
15 an encapsulated bleach.

In a second embodiment, the present invention is directed to a water-soluble sachet comprising a dishwashing composition having:

- 20 (a) a polymer having a weight average molecular weight of greater than about 2,000 and comprising a positive charge; and
(b) a water soluble polymer that reduces phosphate
scale formation, a compound that reduces carbonate
25 scale formation, or both

wherein the dishwashing composition is a gel.

In a third embodiment, the present invention is directed to
30 a method for minimizing spotting and phosphate and/or

- 6 -

carbonate scale formation on glassware being cleaned,
comprising the steps of:

- (a) inserting a water soluble sachet into a dishwashing machine;
- 5 (b) allowing the water soluble sachet to dissolve; and
- (c) subjecting the glassware to a dishwashing composition comprising a polymer comprising a positive charge and a water soluble polymer that reduces phosphate scale formation, a compound that
10 reduces carbonate scale formation, or both.

In a fourth embodiment, the present invention is directed to a package comprising the dishwashing composition described in the first aspect of this invention and instructions not
15 to use a rinse aid composition or conventional water softening salts or both.

As used herein, glassware is defined to include drinking glasses, and any other articles typically found in a
20 commercial or domestic dishwasher. Also, as used herein, water soluble sachet is defined to mean a sachet made of a material that will dissolve, for example, in a cleaning cycle of a domestic dishwasher. Gel, as used herein, is defined to mean any liquid having a viscosity of greater
25 than about 100 cps and less than about 45,000 cps, measured at a shear rate of 1/s at ambient temperature.

The materials that may be used to make the water soluble sachets of this invention include those which may generally
30 be classified as water soluble resins, such as film-forming water soluble resins, either organic or inorganic.

- 7 -

Suitable water-soluble resins which may be used in the invention are described in Davidson and Sittig, *Water-Soluble Resins*, Van Nostrand Reinhold Company, New York (1968), herein incorporated by reference. The water-soluble resin should have proper characteristics such as strength and pliability in order to permit machine handling.

Preferred water-soluble resins include polyvinyl alcohol, cellulose ethers, polyethylene oxide, starch, polyvinylpyrrolidone, polyacrylamide, polyvinyl methyl ether-maleic anhydride, polymaleic anhydride, styrene maleic anhydride, hydroxyethylcellulose, methylcellulose, polyethylene glycols, carboxymethylcellulose, polyacrylic acid salts, alginates, acrylamide copolymers, guar gum, casein, ethylene-maleic anhydride resin series, polyethyleneimine, ethyl hydroxyethylcellulose, ethyl methylcellulose, hydroxyethyl methylcellulose. Lower molecular weight water-soluble, polyvinyl alcohol film-forming resins are generally, preferred.

The generally preferred water-soluble, polyvinyl alcohol film-forming resins should, in addition to low weight average molecular weights, have low levels of hydrolysis in water. Polyvinyl alcohols preferred for use herein have a weight average molecular weight between about 1,000 and about 300,000, and preferably, between about 2,000 and about 150,000, and most preferably, between about 3,000 and about 100,000, including all ranges subsumed therein.

Even further, it is within the scope of this invention to include polyvinyl alcohol films which are copolymers such as

- 8 -

films prepared from vinyl acetate and methacrylic acid precursor monomers. Preferred copolymers typically comprise less than about 15.0% by weight methacrylic acid units in their backbone.

5

When compared to plastics, the tensile strength of polyvinyl alcohol is relatively high, and when compared with other water-soluble materials, the tensile strength of polyvinyl alcohol is extremely high. Reasonable tensile strength is required in film used in sachets of the present invention in order to permit proper handling and machining of the articles. The tensile strength of polyvinyl alcohol will vary with a number of factors, including the percent hydrolysis, degree of polymerization, plasticizer content, and humidity.

15

In a most preferred embodiment, polyvinyl alcohol is used to make the water soluble sachet of this invention, and the dishwashing composition contained therein is substantially free of an unencapsulated compound containing boron, whereby substantially free is defined to mean less than about 2.0% by weight of boron containing compound, based on total weight of the dishwashing composition within the water soluble sachet.

20

25

Polyvinylpyrrolidone, another preferred resin for use to make the sachets of the present invention, may be made from a variety of solvents to produce films which are clear, glossy, and reasonably hard at low humidities. Unmodified films of polyvinylpyrrolidone may be hygroscopic in character. Tackiness at higher humidities may be minimized

30

- 9 -

by incorporating compatible, water-insensitive modifiers into the polyvinylpyrrolidone film, such as 10% of an aryl-sulfonamide-formaldehyde resin.

5 Other preferred water-soluble films may also be prepared from polyethylene oxide resins by standard calendering, molding, casting, extrusion and other conventional techniques. The polyethylene oxide films may be clear or opaque, and are inherently flexible, tough, and resistant to
10 most oils and greases. These polyethylene oxide resin films provide better solubility than other water soluble plastics without sacrificing strength or toughness. The excellent ability to lay flat, stiffness, and sealability of water-soluble polyethylene oxide films make for good machine
15 handling characteristics.

The weight percent of water-soluble, film-forming resin in the final articles of the present invention is from about 0.1% to about 10%, preferably about 0.25% to about 7.5%, and
20 most preferably about 0.50% to about 5%, including all ranges subsumed therein.

As to the dishwashing composition that may be used in this invention, such a composition is a gel having a viscosity
25 from about 100 to about 45,000 cps, and preferably, from about 200 to about 30,000 cps, and most preferably, from about 300 to about 25,000 cps, at ambient temperature, including all ranges subsumed therein.

30 The components of the dishwashing composition of this invention are limited only to the extent that they may be

- 10 -

combined to make a gel having the above-described viscosities and that they do not degrade the structural properties of the film sachet forming materials to an extent where the dishwashing properties of the dishwashing composition are compromised. Typically, such components include water, thickening agent, bleach, buffering agent and builder. Water typically makes up the balance. The dishwashing composition within the water soluble sachet of the present invention can comprise optional ingredients which include colorants, bleach scavengers, perfumes, lime soap dispersants, inert organic molecules, enzymes, enzyme-stabilizers, builders, surfactants, non-encapsulated bleach, anti-foams, anti-tarnish and anti-corrosion agents.

15 In a preferred embodiment the detergent composition used in this invention comprises:

- a) a polymer having a weight average molecular weight of greater than about 2,000 and comprising a positive charge; and
- 20 b) a water soluble polymer that reduces phosphate scale formation, a compound that reduces carborate scale formation, or both.

A polymer comprising a positive charge that may be used in this invention may be defined to mean an entity prepared from at least two monomeric units whereby at least one monomeric unit comprises a positive charge. There generally is no limitation with respect to the type of polymer comprising a positive charge that may be used in this invention other than that the positively charged polymer can be used in a dishwashing composition that comprises a water

- 11 -

soluble polymer that reduces phosphate and/or carbonate scale formation. Such a polymer comprising a positive charge often has a weight average molecular weight of greater than about 2,000; and preferably, greater than about 3,000; and most preferably, greater than about 4,000.

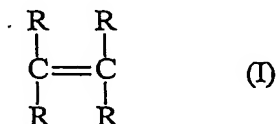
The polymer comprising a positive charge which may be used in this invention is typically soluble or dispersible to at least the extent of 0.01% by weight in distilled water at 25°C. Such a positively charged polymer includes polymers in which one or more of the constituent monomers maintains a positive charge in solution over a portion of the pH range 2-11. A partial listing of the monomers which may be used to make the polymers in this invention are presented in "Water-Soluble Synthetic Polymers: Properties and Behavior, Volume II", by P. Molyneux, CRC Press, Boca Raton, 1983, ISBN 0-8493-6136, the disclosure of which is incorporated herein by reference.

Additional monomers can be found in the "International Cosmetic Ingredient Dictionary, 5th Edition", edited by J.A. Wenninger and G.N. McEwen, The Cosmetic, Toiletry, and Fragrance Association, Washington DC, 1993, ISBN 1-882621-06-9, the disclosure of which is incorporated herein by reference. A third source of such monomers can be found in "Encyclopedia of Polymers and Thickeners for Cosmetics", by R.Y. Lochhead and W.R. Fron, Cosmetics & Toiletries, vol. 108, May 1993, pages 95-135, the disclosure of which is also incorporated herein by reference.

- 12 -

Often, preferred monomers useful to make the polymers comprising a positive charge in this invention may be represented structurally as ethylenically unsaturated compounds having the formula:

5



10

wherein each R is independently a hydrogen, derivatized hydroxy, C₁ to C₃₀ straight or branched alkyl group, aryl, aryl substituted C₁₋₃₀ straight or branched alkyl radical, or a polyoxyalkene condensate of an aliphatic moiety, a heteroatomic organic group comprising at least one positively charged group without a charged nitrogen, quaternized nitrogen atom or at least one amine group comprising a positive charge over a portion of the pH interval 2 to 11, with the proviso that at least one R group is a heteroatomic organic group that has a positive charge without a charged nitrogen, a quaternized nitrogen atom group or an amine group comprising a positive charge.

15
20

Such amine groups can be further delineated as having a pK_a of about 6 or greater, as defined by R. Laughlin in "Cationic Surfactants, Physical Chemistry", edited by D.N. Rubingh and P.M. Holland, Marcel Dekker, New York, 1991, ISBN 0-8247-8357-3. Moreover, it is further noted herein that salts of the monomers represented by formula I may also

25

- 13 -

be used to make the polymers comprising the positive charge in this invention.

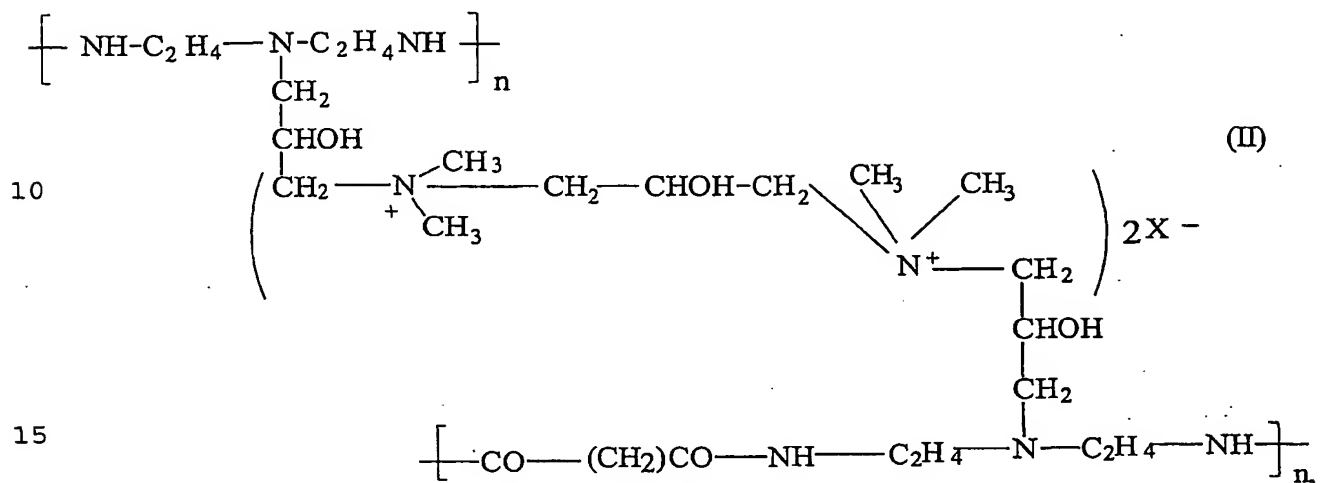
Examples of monomers comprising a positive charge as depicted by formula I include, but are not limited to, 2-vinylpyridine and its 2-vinyl N-alkyl quaternary pyridinium salt derivatives; 4-vinylpyridine and its 4-vinyl N-alkyl quaternary pyridinium salt derivatives; 4-vinylbenzyltrialkylammonium salts such as 4-vinylbenzyltrimethylammonium salt; 2-vinylpiperidine and 2-vinyl piperidinium salt; 4-vinylpiperidine and 4-vinylpiperidinium salt; 3-alkyl 1-vinyl imidazolinium salts such as 3-methyl 1-vinylimidazolinium salt; acrylamido and methacrylamido derivatives such as dimethyl aminopropylmethacrylamide, and methacrylamidopropyl trimethylammonium salt; acrylate and methacrylate derivatives such as dimethyl aminoethyl (meth)acrylate, ethanaminium N,N,N trimethyl 2-[(1-oxo-2 propenyl) oxy] - salt , ethanaminium N,N,N trimethyl 2-[(2 methyl-1-oxo-2 propenyl) oxy] - salt , and ethanaminium N,N,N ethyl dimethyl 2-[(2 methyl-1-oxo-2 propenyl) oxy] - salt.

Also included among the monomers suitable to make the polymers with a positive charge employable in this invention are vinyl amine and vinylammonium salt; diallylamine, and methyldiallylamine.

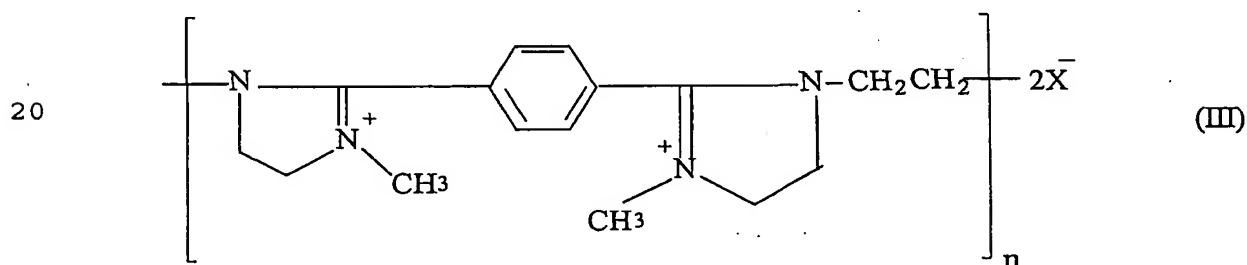
Also, if desired, monomers containing cationic sulfonium salts such as 1-[3-methyl-4-(vinyl-benzyloxy)phenyl] tetrahydrothiophenium chloride may also be used to make the polymers comprising the positive charge of this invention.

Illustrative polymers comprising a positive charge which may be used in this invention include those having a backbone comprising the structural unit:

5



and/or



25

wherein each n is independently 1 to 100,000 and X is chosen from the halides: chloride, bromide, and iodide; or from hydroxide, phosphate, sulfate, hydrosulfate, ethyl sulfate, methyl sulfate, mesylate, tosylate, formate, and acetate.

30

- 15 -

Other positively charged polymers (not the polymerization product of the monomers represented by formula I) suitable for use in this invention are those arising from natural sources and include cocodimethylammonium hydroxypropyl
5 oxyethyl cellulose, lauryldimethylammonium hydroxypropyl oxyethyl cellulose, stearyldimethylammonium hydroxypropyl oxyethyl cellulose, and stearyldimethylammonium hydroxyethyl cellulose; guar 2-hydroxy-3-(trimethylammonium) propyl ether salt; cellulose 2-hydroxyethyl 2-hydroxy 3-(trimethyl
10 ammonio) propyl ether salt.

Still other polymers (not the polymerization product of the monomers represented by formula I) having a positive charge which may be used in this invention include the ionene class
15 of internal positively charged polymers. These polymers are defined by D. R. Berger in "Cationic Surfactants, Organic Chemistry", edited by J.M. Richmond, Marcel Dekker, New York, 1990, ISBN 0-8247-8381-6, herein incorporated by reference.

20

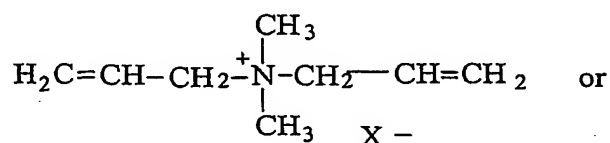
This class of ionene polymers includes co-poly ethylene imine, co-poly ethoxylated ethylene imine and co-poly quaternized ethoxylated ethylene imine; co-poly [(dimethylimino) trimethylene (dimethylimino) hexamethylene
25 disalt], co-poly [(diethylimino) trimethylene (dimethylimino) trimethylene disalt]; co-poly [(dimethylimino) 2-hydroxypropyl salt]; co-polyquaternium-2, co-polyquaternium-17, and co-polyquaternium 18, as defined in the "International Cosmetic Ingredient Dictionary, 5th
30 Edition", edited by J.A. Wenninger and G.N. McEwen.

- 16 -

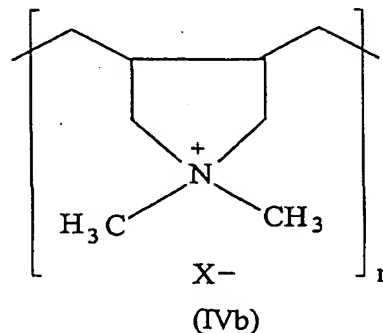
Even other positively charged polymers suitable for use in the present invention include polymers in which one or more of the constituent monomers (precursor monomers) contain at least one positive charge and at least one negative charge over a portion of the pH range 2-11. Such monomers include those comprising formal anionic and cationic charges such as N,N-dimethyl N-acetyl aminoethylmethacrylate. Also included are those polymers derived from monomers which, while not possessing formal charges, have one or more resonance forms which result in the occurrence of fractional positive and negative charges being separated within the monomer.

Such monomers are typified by vinyl pyrrolidone, as described in "Water-Soluble Synthetic Polymers: Properties and Behavior, Volume 1", by P. Molyneux, CRC Press, Boca Raton, 1983, ISBN 0-8493-6135-4, the disclosure of which is incorporated herein by reference.

The preferred polymers comprising a positive charge that may be used in this invention are derived from the polymerization of diallyldimethylammonium salts, having the chemical structure as unpolymerized or polymerized monomer, respectively, of formula IVa or IVb:



(IVa)



(IVb)

- 17 -

wherein n and X are as previously defined.

Still other preferred polymers comprising a positive charge employable in this invention include those polymerized from
5 acrylamidopropyl trimethylammonium salt. Examples of the former preferred polymers are made commercially available by Nalco under the name Merquat Plus 3331. Examples of the latter polymers are developed by Rohm & Haas under the name PC2.

10

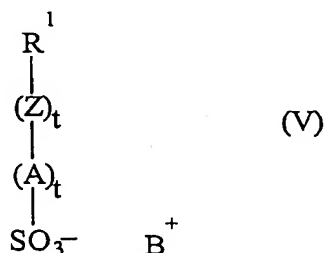
There is no limitation with respect to the amount of polymer with a positive charge that may be used in this invention other than that the amount used results in a dishwashing composition. Typically, however, from about 0.1 to about
15 10.0, and preferably, from about 0.2 to about 7.0, and most preferably, from about 0.3 to about 5.0% by wt. of the dishwashing composition is a polymer comprising a positive charge, based on total weight of the dishwashing composition, including all ranges subsumed therein.

20

In general, the polymers comprising the positive charge which may be used in this invention are typically made commercially available from suppliers like Rhodia, Nalco and Rohm & Haas. The monomers used to make the polymers having
25 a positive charge may be provided by suppliers like Aldrich and Sigma. Such polymers may also be prepared via conventional reactions which include free radical polymerizations.

- 18 -

As to the water soluble polymer that reduces phosphate scale formation, such a polymer often comprises at least one structural unit derived from a monomer having the formula:



wherein R^1 is a group comprising at least one sp^2 bond, Z is O, N, P, S, or an amido or ester link, A is a mono- or a polycyclic aromatic group or an aliphatic group and each t is independently 0 or 1 and B^+ is a monovalent cation.

Preferably, R^1 is a C_2 to C_6 alkene (most preferably ethene or propene). When R^1 is ethenyl, Z is preferably amido, A is preferably a divalent butyl group, each t is 1, and B^+ is Na^+ . Such a monomer is polymerized and sold as Acumer 3100 by Rohm & Haas.

Another preferred embodiment exists when the water soluble polymer is derived from at least one monomer with R^1 as 2-methyl-2-propenyl, Z as oxygen, A as phenylene, each t as 1 and B^+ as Na^+ , and at least one monomer with R^1 as 2-methyl-2-propenyl, each t as 0 and B^+ as Na^+ . Such monomers are polymerized and sold under the name Alcosperse 240 by Alco Chemical.

- 19 -

It is further noted herein that it is within the scope of this invention for all the polymers used to be a homopolymer or copolymer, including terpolymers. Furthermore, the polymers of this invention may be terminated with
5 conventional termination groups resulting from precursor monomers and/or initiators that are used.

There is generally no limitation with respect to how much water soluble polymer that reduces phosphate scale formation
10 is used in this invention as long as the amount used results in a dishwashing composition. Often, from about 0.5% to about 10.0%, and preferably, from about 1.0% to 7.0%, and most preferably, from about 1.5% to about 4.5% by weight water soluble polymer is used, based on total weight of the
15 dishwashing composition, including all ranges subsumed therein. These water soluble polymers typically have a weight average molecular weight from about 1,000 to about 50,000.

20 Regarding the compounds that may be used to reduce carbonate scale formation, these include polyacrylates (and copolymers thereof) having a weight average molecular weight from about 1,000 to about 400,000. Such compounds are supplied by Rohm and Haas, BASF, and Alco Corp. Preferred copolymers include
25 those derived from acrylic acid and maleic acid monomers like Sokalan CP5 and CP7 supplied by BASF, and Acusol 479N, supplied by Rohm & Haas. Copolymers of acrylic acid and methacrylic acid (Colloid 226/35), as supplied by Rhone-Poulenc, may also be used.

30

- 20 -

Other materials that may be used to reduce carbonate scale formation include phosphonate functionalized acrylic acid (Casi 773 as supplied by Buckman laboratories); copolymers of maleic acid and vinyl acetate, and terpolymers of maleic acid, acrylic acid and vinyl acetate (made commercially by Huls); polymaleates (like Belclene 200, as supplied by FMC); polymethacrylates, (like Tomal 850, as supplied by Rohm & Haas); polyaspartates; ethylene diamine disuccinate, organopolyphosphonic acids (and salts thereof) such as sodium salts of amino tri(methylenephosphonic acid), diethylene triamine penta (methylene phosphonic acid); hexamethylene diamine tetramethylene phosphonic acid; ethane 1-hydroxy-1,1-diphosphonic acid (HEDP); organomonophosphonic acids (and salts thereof) such as the sodium salt of 2-phosphono-1,2,4-butane tricarboxylic acid, all of which are sold under the Dequest line as supplied by Solutia.

Phosphates, especially alkali metal tripolyphosphates may also be used as well as mixtures of the above-described materials. It has also been found that combinations of anti-scaling agents can be more effective at reducing calcium carbonate scale than individual anti-scaling agents themselves.

The materials that may be used to reduce carbonate scale formation typically make up from about 0.01% to about 10.0%, and preferably, from about 0.1% to about 6.0 %, and most preferably, from about 0.2% to about 5.0% by weight of the total weight of dishwashing composition, including all ranges subsumed therein.

- 21 -

Any conventional dishwashing builders may be used in this invention. Non-phosphate containing builders such alkali metal salts of polycarboxylic acids may be used (e.g., sodium citrate, iminodisuccinates, oxydisuccinate). Phosphate

5 containing builders are a preferred builder in this invention. Such builders typically make up from about 5.0% to about 75.0% by weight of the total weight of the dishwashing composition, including all ranges subsumed therein. Preferably, however, the amount of phosphate

10 containing builder employed is from about 10.0% to about 70.0%, and most preferably, from about 15.0% to about 65.0% by weight based on total weight of the dishwashing composition and including all ranges subsumed therein.

15 The phosphate containing builders which may be used in this invention are well known, for example, for binding metals such as Ca and Mg ions, both of which are often abundant in hard water found in dishwashing machines. An illustrative list of the phosphate builders which may be used in this

20 invention include sodium, potassium and ammonium pyrophosphate; alkali metal tripolyphosphates, sodium and potassium orthophosphate and sodium polymetaphosphate, with potassium tripolyphosphate (KTP) being especially preferred.

25 Regarding the encapsulated bleach which may be used in this invention, such a bleach (i.e., the core of the encapsulated bleach) includes organic and inorganic peracids as well as salts thereof. Illustrative examples include epsilon phthalimido perhexanoic acid (PAP) and Oxone[®], respectively.

30 The bleaches may be employed with bleach activators, and collectively, the bleach and the activator make up from

- 22 -

about 0.02 wt.% to about 20.0 wt.% of the total weight of the dishwashing composition.

The clad (i.e., outer shell) of the encapsulated bleach is typically a wax such as a paraffin wax. Such paraffin waxes have low melting points, i.e., between about 40°C and about 50°C and a solids content of from about 35% to 100% at 40°C and a solids content of from 0% to about 15% at 50°C. This melting point range for the clad material is desirable for several reasons. The minimum of 40°C generally exceeds any typical storage temperatures that are encountered by cleaning compositions. Thus, the wax coat will protect the core throughout storage of the cleaning composition.

The 50°C melting point cap for the wax clad was selected as providing a wax which will quickly melt or soften early in any automatic dishwashing wash cycle. Melting or softening sufficient to release the core will occur because operating temperatures in automatic dishwashers are usually between 40°C and 70°C. Thus, the paraffin waxes of the invention will release the core material when the capsule is exposed to the warmed wash bath, but not before. Paraffin waxes are selected over natural waxes for the subject invention because in liquid alkaline environments, natural waxes hydrolyze and are unstable. Moreover, melted paraffin waxes of the encapsulated bleaches used in the invention will remain substantially molten at 40°-50°C. Such molten wax is easily emulsified by surfactant elements in cleaning compositions. Consequently, such waxes will leave less undesirable waxy residue on items to be cleaned than waxes with higher melting points.

- 23 -

Thus, the wax coat preferably does not include any paraffins having a melting point substantially above 50°C, lest the higher melting point components remain solid throughout the wash cycle and form unsightly residues on surfaces to be cleaned nor any paraffins with solid contents discussed below.

The distribution of solids of the paraffin waxes of the invention ensures storage integrity of the encapsulated particles at temperatures up to 40°C in either a liquid or moist environment while yielding good melting performance to release its active core during use at temperatures of about 50°C.

The amount of solids in a wax at any given temperature as well as the melting point range may be determined by measuring the latent heat of fusion of each wax by using Differential Scanning Calorimetry (DSC) by a process described in Miller, W.J. et al. Journal of American Oil Chemists' Society, July, 1969, V. 46, No. 7, pages 341-343, incorporated by reference. This procedure was modified as discussed below. DSC equipment used in the procedure is preferably the Perkin Elmer Thermoanalysis System 7 or the Dupont Instruments DSC 2910.

Specifically, the DSC is utilized to measure the total latent heat of fusion of multi-component systems which do not have a distinct melting point, but rather, melt over a temperature range. At an intermediate temperature within this range one is capable of determining the fraction of the

- 24 -

latent heat required to reach that temperature. When acquired for a multi-component mixture of similar components such as commercial waxes, this fraction correlates directly to the liquid fraction of the mixture at that temperature.

5 The solids fraction for the waxes of interest are then measured at 40°C and 50°C by running a DSC trace from -10°C to 70°C and measuring the fraction of the total latent heat of fusion required to reach these temperatures. A very low temperature ramping rate of 1°C/min should be used in the
10 test to ensure that no shifting of the graph occurs due to temperature gradients within the sample.

The more solids present in a wax at room temperature, the more suitable the wax is for the present invention; this is
15 because such solids strengthen the wax coating, rendering the particle less vulnerable to ambient moisture or a liquid aqueous environment, whereas "oil" or liquid wax softens the wax, opening up pores in the coating and thereby provides poorer protection for the core of the particle. Significant
20 solid paraffin remaining at 50°C may remain on the cleaned hard surfaces (e.g., dishware in an automatic dishwashing machine) and is undesirable.

Therefore, the wax solids content as measured by
25 Differential Scanning Calorimetry for suitable paraffin waxes may range from 100% to about 35%, optimally from 100% to about 70%, at 40°C and from 0% to about 15% and preferably 0% to about 5% at 50°C.

30 Particles coated with micro-crystalline waxes would therefore have a poorer protective coating, and the wax coat

- 25 -

which melts from such particles would be less likely to emulsify in cleaning compositions. Thus, micro-crystalline wax are not considered within the operative scope of this invention.

5

Commercially available paraffin waxes which are suitable for encapsulating the solid core materials include Merck 7150 (54% solids content at 40°C and 2% solids content at 50°C) ex. E. Merck of Darmstadt, Germany; IGI 1397 (74% solids
10 content at 40°C and 0% solids content at 50°C) and IGI 1538 (79% solids content at 40°C and 0.1% solids content at 50°C ex. The International Group, Inc. of Wayne, PA; and Ross fully refined paraffin wax 115/120 (36% solids content at 40°C and 0% solids content at 50°C) ex Frank D. Ross Co.,
15 Inc. of Jersey City, NJ. Most preferred is IGI 1397.

Mixtures of paraffin waxes with other organic materials such as polyvinyl ethers as described in U.S. Patent Nos. 5,460,743 and 5,589,267 are also useful to make the clads of
20 this invention.

Other bleaches which may be used in this invention include hydrogen peroxide and its precursors (e.g., sodium perborate and sodium percarbonate), alkyl, aryl and acyl peroxides
25 such as benzoyl peroxide and solid chlorine bleach sources such as dichloroisocyanurate.

When preparing the encapsulated bleaches employable in this invention, such an encapsulated particle is made via well
30 known art recognized techniques which include spraying molten wax onto bleach particles in a fluidized bed. A

- 26 -

preferred process is described in U.S. Patent No. 5,230,822. Encapsulating bleach is preferred in this invention since the clad prevents interactions between the bleach and film forming resin during storage of the sachets.

5

If desired, conventional bleach activators (including catalysts) may be used with the bleaches described herein. These activators include (6-nonamidocaproxy) oxybenzene sulfonate (as described in EPO 170,386) N,N,N',N'-

10 tetraacetylenediamine, nonanoyloxybenzenesulfonate, cationic nitriles, cholyl(4-sulfohenyl)carbonate, and quaternary imine salts (e.g., N-methyl-3,4-dihydroisoquinolinium p-toluenesulfonate).

15 Other bleach activators which may be used include transition metal-containing bleach catalysts such as $[\text{Mn}^{\text{IV}}_2(\mu\text{-O})_3(\text{Me}_3\text{TACN})_2](\text{PF}_6)_2$ (as described in U.S. Patent Nos. 4,728,455, 5,114,606, 5,153,161, 5,194,416, 5,227,084, 5,244,594, 5,246,612, 5,246,621, 5,256,779, 5,274,147, 20 5,280,117), $[\text{Fe}^{\text{II}}(\text{MeN}_4\text{py})(\text{MeCN})](\text{ClO}_4)_2$ (as described in EP 0 909 809) and $[\text{Co}^{\text{III}}(\text{NH}_3)_5(\text{OAc})](\text{OAc})_2$ (as described in U.S. Patent No. 5,559,261, WO 96/23859, WO 96/23860, WO 96/23861). It is further noted that the bleach activators employable in this invention may be added to the dishwashing composition as 25 granulates or encapsulated granulates or both.

It is also within the scope of this invention to employ (optionally) conventional dishwashing enzymes. The enzymes typically make up from about 0.5% to about 10.0% by weight 30 of the total weight of the dishwashing composition and

- 27 -

include proteases like Savinase[®], Purafect Ox[®], Properase[®], and Ovozyme[®] and amylases like Termamyl[®], Purastar ST[®], Purastar Ox Am[®], and Duramyl[®], all of which are commercially available.

5

The buffering agents which may be used typically make up from about 1.0% to about 25.0% by weight of the total weight of the dishwashing composition and include well known buffering agents like potassium and sodium salts of disilicate; bicarbonate and carbonate. Conventional dishwashing surfactants may also (optionally) be employed in this invention and these include anionic surfactants like alkyl sulfates and sulfonates as well as fatty acid ester sulfonates. Particularly, salts of (i.e., sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) anionic sulfates, sulfonates, carboxylates, and sarcosinates may be used.

10

15

Other optional anionic surfactants which may be used include isothionates, like acyl-isothionates, N-acyltaurates, fatty acid amides of methyl tauride, alkyl succinates and sulfosuccinates; mono esters of sulfosuccinate; and diesters of sulfosuccinate. These types of surfactants often make up from about 0.0% to about 10.0% by weight of the total weight of the dishwashing composition.

20

25

Suitable optional antifoaming agents for use herein may comprise essentially any known antifoam compound, including, for example, silicone antifoams, silicone oil, mono- and distearyl acid phosphates, mineral oil, and 2-alkyl and

30

- 28 -

alcanol antifoam compounds. These antifoaming agents may be used in combination with defoaming surfactants. The dishwashing composition typically comprises from about 0.02% to 2% by weight of antifoaming agent, preferably, 0.05% to 1.0%.

In an especially preferred embodiment, anti-tarnishing agents may be used in this invention. Such anti-tarnishing agents typically comprise benzotriazole, 1,3 N-azoles, isocyanuric acid, purine compounds, and mixtures thereof.

When preparing the dishwashing composition of this invention, the desired components (e.g., polymer comprising a positive charge and water soluble polymer) or solutions thereof are mixed, and added to a solution of the thickening agent. The order of addition of ingredients can be varied. The amount of water present in the detergent composition is typically from about 15% to about 80%, and preferably from about 20% to about 75% and most preferably from about 25% to about 70% by weight, based on total weight of the detergent composition, including all ranges subsumed therein.

The thickeners which may be used in this invention include cross-linked anionic polymers. Illustrative examples include cross-linked polyacrylic acid-type thickening agents which are sold by B.F. Goodrich under their Carbopol trademark. Especially preferred are Carbopol 934, 940, 941, 980 and 981.

The amount of the high molecular weight, cross-linked polyacrylic acid or other high molecular weight, hydrophilic

- 29 -

cross-linked polyacrylic acid-type thickening agent to impart the desired rheological property of linear viscoelasticity will generally be in the range of from about 0.1% to 3.0%, and preferably, from about 0.2% to 2.0% by weight based on the weight of the composition. It is also noted that thickening agents that are not bleach resistant may also be employed with the sachets of the present invention.

10 Other optional additives which may be used with the preferred embodiments of this invention include well known items such as perfumes, antifoaming agents, anti-tarnish agents, dispersants, colorants, lime soap dispersants, inert organic molecules, enzyme stabilizers, non-encapsulated
15 bleaches and bleach scavengers. Such additives, collectively, do not normally make up more than about 8.0% by weight of the total weight of the dishwashing composition.

20 In an especially preferred embodiment, the dishwashing compositions used in the water soluble sachets of this invention further comprise a surfactant having a cloud point in water of less than about 60°C. Such a surfactant typically enhances wetting properties of the glassware being
25 cleaned. These surfactants (typically nonionic) can be broadly defined as surface active compounds with at least one uncharged hydrophilic substituent.

A major class of such nonionic surfactants are those
30 compounds produced by the condensation of alkylene oxide groups with an organic hydrophobic material which may be

- 30 -

aliphatic or alkyl aromatic in nature. The length of the hydrophilic or polyoxyalkylene radical which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements.

Illustrative examples of various suitable nonionic surfactant types are polyoxyalkylene condensates of aliphatic carboxylic acids, whether linear- or branched-chain and unsaturated or saturated, especially ethoxylated and/or propoxylated aliphatic acids containing from about 8 to about 18 carbon atoms in the aliphatic chain and incorporating from about 2 to about 50 ethylene oxide and/or propylene oxide units. Suitable carboxylic acids include "coconut" fatty acids (derived from coconut oil) which contain an average of about 12 carbon atoms, "tallow" fatty acids (derived from tallow-class fats) which contain an average of about 18 carbon atoms, palmitic acid, myristic acid, stearic acid and lauric acid.

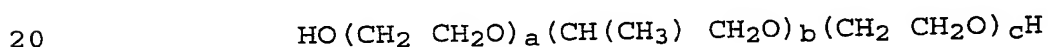
Other nonionic surfactants having a cloud point of less than about 60°C include polyoxyalkylene condensates of aliphatic alcohols, whether linear- or branched-chain and unsaturated or saturated, especially ethoxylated and/or propoxylated aliphatic alcohols containing from about 6 to about 24 carbon atoms and incorporating from about 2 to about 50 ethylene oxide and/or propylene oxide units. Suitable alcohols include "coconut" fatty alcohol, "tallow" fatty alcohol, lauryl alcohol, myristyl alcohol and oleyl alcohol. Preferred examples of such materials are provided by BASF

- 31 -

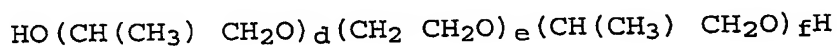
Corporation as a series under the tradename Plurafac. Particularly preferred surfactants are Plurafac LF 301, Plurafac LF 403 and Plurafac SLF-18. Also included within this class of nonionic surfactants are epoxy capped
5 poly(oxyalkylated) alcohols as described in WO 94/22800. A preferred example of this class of material is poly-tergent SLF 18B 45 made available by BASF Corporation.

10 Polyoxyethylene or polyoxypropylene condensates of alkyl phenols, whether linear- or branched-chain and unsaturated or saturated, containing from about 6 to 12 carbon atoms and incorporating from about 2 to about 25 moles of ethylene oxide and/or propylene oxide are other types of nonionic surfactants which may be used.

15 Other desired nonionic surfactants which may be used include polyoxyethylene-polyoxypropylene block copolymers having formulae represented as



or



wherein a, b, c, d, e and f are integers from 1 to 350
25 reflecting the respective polyethylene oxide and polypropylene oxide blocks of said polymer. The polyoxyethylene components of the block polymer constitutes at least about 10% of the block polymer. The material preferably has a molecular weight of between about 1,000 and
30 15,000, more preferably from about 1,500 to about 6,000.

- 32 -

These materials are well known in the art. They are available as a series of products under the trademark "Pluronic" and "Pluronic R", from the BASF Corporation.

5

It is also noted herein that while the surfactants for enhancing wetting properties of this invention typically have a cloud point of less than about 60°C, they preferably have a cloud point of less than about 50°C, and most
10 preferably, less than about 45°C.

The surfactants having a cloud point in water of less than about 60°C are typically present within the dishwashing composition at levels of at least 0.5 wt.%, preferably, 1-15
15 wt.%, and most preferably, 1.5 to 8 wt.%, based on the total weight of the dishwashing composition, including all range subsumed therein.

When washing glassware with the dishwashing composition of
20 this invention, soiled glassware is typically placed in a conventional domestic or commercial dishwashing machine as is the dishwashing composition of this invention (in no particular order). The dishwashing composition of this invention then dissolves in the water (as does the sachet
25 comprising it) of the dishwasher to wash the glassware. The typical dishwashing cycle is from about 10 minutes until about 60 minutes and the typical temperature of the water in the dishwasher is from about 40°C to about 70°C. The glassware resulting from the above-described cleaning method
30 is clean and has an excellent glass appearance (i.e., substantially free of film and spots). Such results are

- 33 -

unexpectedly obtained even when hard water at high temperatures (greater than 55°C) is used, in the absence of rinse aid compositions.

5 When marketing the superior dishwashing composition of this invention, it is preferred that the dishwashing composition is a gel, as described above, and sold in a package with directions to add the dishwashing composition to the dishwashing machine as a 3-in-1 product. Thus, a dishwasher
10 is charged with the dishwashing composition of this invention without having to add to the dishwasher conventional rinse aid compositions and sodium chloride.

When preparing the actual water soluble sachets of the
15 present invention, any of the art recognized techniques for making water soluble sachets may be used.

One particularly preferred method for pressing the actual water soluble sachets of the present invention employ
20 thermoformed packages. The thermoforming process generally involves molding a first sheet of water soluble film to form one or more recesses adapted to retain the gel of the current invention, placing the gel in at least one recess, placing a second sheet of water soluble material over the
25 first so as to cover each recess, and heat sealing the first and second sheets together at least around the recesses so as to form one or more water soluble packages as described in WO 00/55415.

30 A second route comprises vertical form-fill-seal (VFFS) envelopes. In one of the VFFS processes, a roll of water

- 34 -

soluble film is sealed along its edges to form a tube, which tube is heat sealed intermittently along its length to form individual envelopes which are filled with gel and heat sealed.

5

The size and the shape of the sachet are not limited and individual sachets may be connected via perforated resin. Preferably, the sachet is of the size to carry a unit dose for a domestic dishwashing machine.

10

The following examples are provided to facilitate an understanding of the present inventions. The examples are not intended to limit the scope of the inventions as described in the claims.

15

Examples 1-9 depict detergent compositions (all parts by weight) with encapsulated bleaches that can be filled into the sachets in the described inventions.

- 35 -

Examples 1-9

| Example | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|-----------------------|-----|-----|-----|------|------|-----|-----|-----|-----|
| Carbopol 627 | 1.5 | | | | | | | | |
| Carbopol 980 | | 1.5 | 1 | 1.5 | 0.8 | | 1.5 | 1.5 | 1.5 |
| Carbopol 941 | | | | | | 1 | | | |
| KTP | 30 | | 31 | 29.5 | 27.4 | 29 | 30 | 28 | 30 |
| Sodium citrate | | 30 | | | | | | | |
| Potassium carbonate | | | | | | 8 | | | |
| Potassium bicarbonate | | | | | 7.6 | | | 8 | |
| Glycerol | 6 | 6 | 6.8 | 6.4 | 6 | 6 | 7.5 | 7.5 | 6 |
| NaOH | | 0.8 | | | | | | | |
| KOH | 0.8 | | 0.7 | 1 | 0.6 | | 0.6 | 0.8 | 0.8 |
| Sokalan CP7 | 5 | 5 | | | | | | | |
| Sokalan PA25 PN | | | 3.8 | 3.6 | 3.4 | 3.7 | 3.7 | | 3.7 |
| Na HEDP | | | 0.8 | 0.8 | 0.7 | 0.8 | 0.8 | 1.1 | 0.8 |
| Sodium sulfite | 0.1 | 0.1 | 0.2 | 0.2 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| Plurafac LF403 | 2 | 2 | 2.1 | 2 | 1.9 | 4.5 | 2 | 4 | 2 |
| Bleach (PAP capsules) | 4.3 | 4.3 | 4.6 | 9.2 | 9.2 | 4.3 | 4.3 | 4.3 | 4.3 |
| Amylase | 0.4 | 0.4 | 0.7 | 0.7 | 0.7 | 0.4 | 0.4 | 0.4 | 0.4 |
| Protease | 0.6 | 0.6 | 1.6 | 1.6 | 1.6 | 0.6 | 0.6 | 0.6 | 0.6 |
| Alcosperse 240 | | | | | | | 2 | 2 | 2 |
| Acusol 460 | | | | | | | 2 | | |
| Merquat 3331 | | | | | | | | 0.8 | 0.8 |
| Sodium lauryl sulfate | | | 1.4 | 1.3 | 1.2 | | | | 2 |
| Antifoam | | | 1.6 | 1.6 | 1.5 | | | | 0.6 |

Examples 1-9 depict samples of detergent compositions with
5 encapsulated bleaches that can be filled into sachets.

All sachets, for purposes of these nine (9) examples were
made with polyvinyl alcohol (PVA) comprising film (Chris
Craft M8630).

10

Example 10

Cleaning experiments were carried out in Bauknecht GSF
4741dishwasher using the 50 BIO(N) program. 33g of
15 detergent, as described in example 5, was sealed within a

- 36 -

sachet. The pouch was placed in the dispenser of the machine. Water used for the experiment was adjusted to 300ppm permanent hardness with $\text{Ca:Mg} = 4:1$ and NaHCO_3 adjusted to 320ppm. Soils used included: 4 ceramic plates coated with 2.0g egg yolk on each plate; 4 stainless steel plates coated with 2.0g each of egg yolk; 4 ceramic plates coated with 2.0g ea. of potato starch soil; 4 ceramic plates coated with 2.0g ea. of cream of wheat; ; 4 ceramic plates coated with 2.0g ea. of roux soil; 40g of ASTM butter-milk soil; 6 cups with 3x tea stain.

Eight (8) clean glasses were placed onto the top rack of dishwasher. Teacups were visually assessed for residual tea stain and scored on a scale of 0-5 with a score of 0 indicating 100% cleaned while 5 represents unwashed cups. The egg plates were visually examined for residual soil, and were then scored on a scale from 0 (no residual soil) to 100 (100% area covered with soil), while wheat and roux plates were dipped in an iodine bath to expose residual soil and scored on a 0 -100 scale similar to the egg soil. The scores reported in example 10 are average scores of each type of soil.

| Example 10 | Tea | Egg-Ceramic | Egg-Steel | Wheat | Roux |
|------------|-----|-------------|-----------|-------|------|
| Score | 2.1 | 0 | 0 | 0 | 10 |

As can be seen by example 10, the dishwashing gel composition with an encapsulated bleach enclosed in a water soluble sachet provided excellent cleaning results, and no evidence of undissolved polyvinyl alcohol comprising film was seen.

- 37 -

Examples 11-12

33g of a gel formulation corresponding to composition described in example 11 was sealed in a PVA sachet. A
 5 16.62g tablet corresponding to an equivalent composition described in example 12 was pressed.

| | Example 11 (Gel in sachet) | | Example 12 (Tablet) |
|-----------------------------|----------------------------|---------------|---------------------|
| | g/dose | g active/dose | g/dose |
| Carbopol 980 (4% soln.) | 9.43 | 0.38 | |
| KTP | 8.81 | 8.81 | 8.81 |
| SLS (30% soln.) | 1.10 | 0.33 | |
| SLS granules | | | 0.33 |
| Antifoam emulsion | 0.44 | 0.44 | 0.44 |
| Glycerol | 1.89 | 1.89 | |
| Sokalan PA25-PN (54% soln.) | 1.95 | 1.05 | |
| Sokalan PA25-CL | | | 1.05 |
| HEDP | 0.22 | 0.22 | 0.22 |
| Sodium sulfite | 0.03 | 0.03 | 0.03 |
| Plurafac LF 403 | 0.63 | 0.63 | 0.63 |
| Potassium bicarbonate | 2.20 | 2.20 | 2.20 |
| KOH | 0.35 | 0.35 | |
| Alcosperse 240 (44% soln.) | 1.20 | 0.53 | |
| Alcosperse 240- dried | | | 0.53 |
| Merquat 3331 (10% soln.) | 2.64 | 0.26 | |
| Merquat 3331-dried | | | 0.26 |
| PAP capsules | 1.42 | 1.42 | 1.42 |
| Ovozyme | 0.50 | 0.50 | 0.50 |
| Duramyl | 0.20 | 0.20 | 0.20 |
| Total dose | 33.00 | | 16.62 |

10 Example 13-14

One wash tests were done in a Bauknecht GSF 4741 dishwasher using the 50 BIO(N) program. The detergent sachet (example 13) or the tablet (example 14) were placed in the dispenser

- 38 -

of the machine. Water used for the experiment was adjusted to 300ppm permanent hardness with Ca:Mg = 4:1 and NaHCO₃ adjusted to 320ppm. 40g of buttermilk soil on the door of the dishwasher and 5g of egg yolk were added prior to the run. A full clean dish load, with 8 glasses, was included for scoring. At the end of the run, glasses were scored for spotting and filming. Both spotting and filming scores were recorded based on area covered by, and intensity of the spots and film. The scores are expressed on a 0 to 5 scale, 0 being completely free of spots or film.

| Example | <u>Dose</u> | Spots | Film | Total |
|---------|-------------|-------|------|-------|
| 13 | Example 11 | 0.3 | 1.4 | 1.7 |
| 14 | Example 12 | 1.1 | 1.3 | 2.4 |

As can be seen by a comparison of examples 13 and 14 there is a significant performance advantage when the formulation is dosed as a gel in a soluble sachet than when dosed as a tablet.

Examples 15-17

Tests to monitor the anti-spotting and anti-filming efficacy of formulations were performed (as described in examples 15-16) in a Miele G656 machine, using a 55°C Normal cleaning cycle and a water hardness of 400/320 ppm. The sachets containing 33 g of formulation (made per example 1) were dosed via the dispenser and the polymer additives were dosed

- 39 -

as either aqueous solutions (Example 16) or as solids (Example 17) at the time of cup opening.

| Example | Dose | Spots | Film | Total |
|---------|---|-------|------|-------|
| 15 | 1 sachet | 1.4 | 0.9 | 2.3 |
| 16 | 1 pouch + 2.7g Merquat 3331 (10% active) + 1.23g Alcosperse 240 (44% active) | 0.0 | 1.0 | 1.0 |
| 17 | 1 pouch + 0.27g Merquat 3331 (solid) + 0.54g Alcosperse 240-D (solid) | 0.4 | 1.6 | 2.0 |

5

As can be seen by a comparison of Examples 15-17 there is a significant performance advantage when the polymers are dosed in the liquid form rather than as dried solids.

- 40 -

CLAIMS

1. A water soluble sachet comprising a dishwashing composition wherein the dishwashing composition comprises an encapsulated bleach.
5
2. The water soluble sachet according to claim 1 wherein the dishwashing composition is a gel.
- 10 3. The water soluble sachet according to claim 2 wherein the gel has a viscosity greater than about 100 cps and less than about 45,000 cps.
4. The water soluble sachet according to any one of the preceding claims wherein the encapsulated bleach comprises a clad with a paraffin wax and a core with a bleach.
15
5. The water soluble sachet according to any one of the preceding claims wherein the water soluble sachet comprises polyvinyl alcohol and the dishwashing composition is substantially free of an unencapsulated compound containing boron.
20
6. A water soluble sachet comprising a dishwashing composition having:
25
 - (a) a polymer having a weight average molecular weight of greater than about 2,000 and comprising a positive charge; and
 - (b) a water soluble polymer that reduces phosphate scale formation, a compound that reduces carbonate scale formation, or both
30

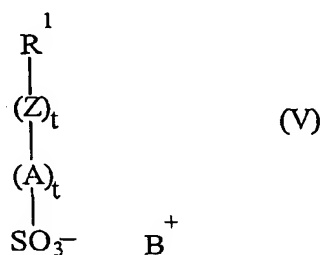
- 41 -

wherein the dishwashing composition is a gel.

7. The water soluble sachet according to claim 6 wherein the dishwashing composition further comprises a surfactant
5 having a cloud point in water of less than about 60°C.

8. The water soluble sachet according to claim 7 wherein the polymer that reduces phosphate scale formation is derived from a monomer having the formula:

10



15

wherein R^1 is a group comprising at least one sp^2 bond, Z is O, N, P, S, or an amido or ester link, A is a mono- or a
20 polycyclic aromatic group or an aliphatic group and each t is independently 0 or 1 and B^+ is a monovalent cation.

9. The water soluble sachet according to any one of claims 6 to 8 wherein the compound that reduces carbonate scale
25 formation is a polyacrylic acid, a copolymer derived from acrylic and maleic acid, a copolymer of acrylic acid and methacrylic acid, a phosphonic acid, polyphosphoric acid, or salts thereof or mixtures thereof.

- 42 -

10. The water soluble sachet according to any one of claims 6 to 9 wherein the polymer comprising a positive charge is derived from acrylamidopropyl trimethylammonium salt or diallyldimethylammonium salt.

5

11. The water soluble sachet according to any one of claims 6 to 10 wherein the dishwashing composition comprises an encapsulated bleach.

10 12. The water soluble sachet according to anyone of claims 6 to 11 wherein the dishwashing composition is substantially free of unencapsulated compounds containing boron.

13. A package comprising:
15 a water soluble sachet comprising a dishwashing composition wherein the dishwashing composition is a gel which comprises an encapsulated bleach.

14. The package according to claim 13 wherein the package
20 further comprises instructions not to use a rinse aid composition or conventional water softening salts or both.

15. The package according to claim 13 or claim 14 wherein the dishwashing composition comprises:
25 (a) a polymer having a weight average molecular weight of greater than about 2,000 and comprising a positive charge; and
(b) a water soluble polymer that reduces phosphate scale formation, a compound that reduces carbonate
30 scale formation, or both
wherein the dishwashing composition is a gel.

- 43 -

16. The package according to claim 15 wherein the dishwashing composition further comprises a surfactant having a cloud point in water of less than about 60°C.

5 17. The package according to claim 15 or claim 16 wherein the polymer that reduces phosphate scale formation is derived from a monomer having the formula:



15 wherein R^1 is a group comprising at least one sp^2 bond, Z is O, N, P, S, or an amido or ester link, A is a mono- or a polycyclic aromatic group or an aliphatic group and each t is independently 0 or 1 and B^+ is a monovalent cation.

20 18. The package according to any one of claims 15 to 17 wherein the compound that reduces carbonate scale formation is a polyacrylic acid, a copolymer derived from acrylic and maleic acid, a copolymer of acrylic acid and methacrylic acid, a phosphonic acid, polyphosphoric acid, or salts thereof or mixtures thereof.

25

19. A method for minimizing spot and film formation, and phosphate and/or carbonate scale formation on glassware being cleaned, comprising the steps of:

30 (a) inserting a water soluble sachet into a dishwashing machine;

- 44 -

(b) allowing the water soluble sachet to dissolve; and

(c) subjecting the glassware to a dishwashing
composition comprising a polymer comprising a positive
charge, and a water soluble polymer that reduces
5 phosphate scale formation, a compound that reduces
carbonate scale formation, or both.

20. The method according to claim 19 wherein the
dishwashing composition is a gel having a viscosity greater
10 than about 100 cps and less than about 45,000 cps.

21. The method according to claim 19 or claim 20 wherein
the dishwashing composition comprises an encapsulated
bleach.

15

22. The method according to claim 21 wherein the
dishwashing composition is substantially free of an
unencapsulated compound containing boron.

20

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
26 September 2002 (26.09.2002)

PCT

(10) International Publication Number
WO 02/074891 A3

(51) International Patent Classification: **C11D 17/04,**
3/39, 3/395

Noortlaan 120, NL-3133 AT Vlaardingen (NL). **SECEM-SKI, Isaac, Israel;** Unilever Research U.S. Inc., 45 River Road, Edgewater, NJ 07020 (US).

(21) International Application Number: **PCT/EP02/02770**

(22) International Filing Date: 11 March 2002 (11.03.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
09/810,106 16 March 2001 (16.03.2001) US

(71) Applicant (for AE, AG, AU, BB, BZ, CA, CY, GB, GD, GH, GM, IE, IL, KE, LC, LK, LS, MN, MW, NZ, OM, SD, SG, SL, SZ, TT, TZ, UG, ZA, ZM, ZW only): **UNILEVER PLC** [GB/GB]; Unilever House, Blackfriars, London EC4P 4BQ (GB).

(71) Applicant (for AL, AM, AT, AZ, BA, BE, BG, BR, BY, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, FR, GE, GR, HR, HU, ID, IS, IT, JP, KG, KP, KR, KZ, LR, LT, LU, LV, MA, MC, MD, MG, MK, MX, MZ, NL, NO, PH, PL, PT, RO, RU, SE, SI, SK, TJ, TM, TN, TR, UA, UZ, VN, YU only): **UNILEVER NV** [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).

(71) Applicant (for IN only): **HINDUSTAN LEVER LIMITED** [IN/IN]; Hindustan Lever House, 165/166 Backbay Reclamation, Maharashtra, Mumbai 400 020 (IN).

(72) Inventors: **PFEIFFER, Natasha;** 235 West 100th Street, Apartment 2F, New York, NY 10025 (US). **GHATLIA, Naresh, Dhirajlal;** LFEDC Vlaardingen, Olivier van

(74) Agents: **MULDER, Cornelis, Willem, Reinier et al.;** Unilever PLC, Patent Department, Colworth House, Sharnbrook, Bedford, Bedfordshire MK44 1LQ (GB).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZM, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

(88) Date of publication of the international search report:
30 January 2003

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: **WATER SOLUBLE SACHET WITH A DISHWASHER COMPOSITION**

(57) Abstract: This invention is directed to a water soluble sachet comprising a detergent composition having an encapsulated bleach. The water soluble sachet unexpectedly results in excellent cleaning properties and minimizes spot and film formation on items being cleaned in a dishwasher.

WO 02/074891 A3

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 02/02770

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C11D17/04 C11D3/39 C11D3/395

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|--|-----------------------|
| X | WO 98 30670 A (HINTON GERALD THOMAS) 16 July 1998 (1998-07-16) claims 1-7,9-12 example 5 | 1,5 |
| X | WO 00 02980 A (HINTON GERALD THOMAS) 20 January 2000 (2000-01-20) claims 1-9,11-13 example 2 | 1,5 |
| Y | US 4 115 292 A (MUELLER FRANK J ET AL) 19 September 1978 (1978-09-19) claims 1,5-7,9-11 examples I-XXVIII column 10, line 31 - line 35 | 1-5,13, 14 |
| | --- -/- | |

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "A" document member of the same patent family

Date of the actual completion of the international search

29 July 2002

Date of mailing of the international search report

27. 11. 2002

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Neys, P

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 02/02770

| C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT | | |
|--|--|---------------------------|
| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
| Y A | EP 0 596 550 A (UNILEVER NV) 11 May 1994 (1994-05-11) claims 1,8,16 examples page 2, line 50 - line 54 page 3, line 45 -page 4, line 11 --- | 1-5,13, 14 15,16,18 |
| Y | US 5 141 664 A (CORRING ROBERT ET AL) 25 August 1992 (1992-08-25) claim 1 examples column 7, line 39 -column 8, line 68 --- | 1-5,13, 14 |
| Y A | EP 0 846 757 A (UNILEVER PLC) 10 June 1998 (1998-06-10) claims 1,7,10 example 1 page 8, line 11 - line 22 --- | 1-4,13, 14 15,16,18 |
| A | EP 0 893 491 A (UNILEVER PLC) 27 January 1999 (1999-01-27) claims page 2, line 38 -page 3, line 34 page 4, line 30 -page 5, line 5 page 10, line 17 - line 35 page 10, line 56 -page 11, line 1 examples A,C --- | 1-5, 13-18 |
| A | WO 99 58633 A (UNILEVER PLC) 18 November 1999 (1999-11-18) claims table 1 page 7, line 23 -page 17, line 16 page 22, line 33 - line 35 page 38, line 7 -page 39, line 15 ----- | 13-18 |

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP 02/02770

Box I Observations where certain claims were found unsearchable (Continuation of Item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of Item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
Claims 1-5, 13-18.

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-5,13-18

A water soluble sachet comprising a dishwashing composition comprising an encapsulated bleach. A package comprising this sachet and this dishwashing composition in gel form and a method for cleaning glassware by using this sachet.

2. Claims: 6-12,19-22

A water soluble sachet comprising a dishwashing gel having (a) a polymer with average molecular weight of greater than about 2,000 and comprising a positive charge; and (b) a water soluble polymer for reducing phosphate scale formation and/or a compound for reducing carbonate scale formation. A method for cleaning glassware by using this sachet.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 02/02770

| Patent document cited in search report | | Publication date | Patent family member(s) | Publication date |
|---|---|---------------------|--|--|
| WO 9830670 | A | 16-07-1998 | AT 224439 T AU 738231 B2 AU 5567898 A DE 69808049 D1 EP 0958347 A2 WO 9830670 A2 JP 2001508100 T NZ 335308 A US 6465413 B1 | 15-10-2002 13-09-2001 03-08-1998 24-10-2002 24-11-1999 16-07-1998 19-06-2001 28-02-2000 15-10-2002 |
| WO 0002980 | A | 20-01-2000 | AT 224944 T AU 4631099 A CA 2337069 A1 DE 69903185 D1 EP 1121410 A2 WO 0002980 A2 NZ 509670 A | 15-10-2002 01-02-2000 20-01-2000 31-10-2002 08-08-2001 20-01-2000 01-03-2002 |
| US 4115292 | A | 19-09-1978 | NONE | |
| EP 0596550 | A | 11-05-1994 | US 5336430 A CA 2108985 A1 EP 0596550 A2 JP 6200297 A | 09-08-1994 04-05-1994 11-05-1994 19-07-1994 |
| US 5141664 | A | 25-08-1992 | NONE | |
| EP 0846757 | A | 10-06-1998 | CA 2221955 A1 EP 0846757 A2 | 05-06-1998 10-06-1998 |
| EP 0893491 | A | 27-01-1999 | US 5981456 A AU 8864298 A BR 9811023 A WO 9905248 A1 EP 0893491 A1 EP 0998548 A1 US 6239091 B1 US 6281180 B1 ZA 9806488 A | 09-11-1999 16-02-1999 19-09-2000 04-02-1999 27-01-1999 10-05-2000 29-05-2001 28-08-2001 21-01-2000 |
| WO 9958633 | A | 18-11-1999 | US 6239091 B1 AU 8864298 A AU 9258498 A BR 9811023 A BR 9815849 A CA 2327308 A1 WO 9905248 A1 WO 9958633 A1 EP 0998548 A1 EP 1078032 A1 HU 0101860 A2 TR 200003308 T2 ZA 9806483 A | 29-05-2001 16-02-1999 29-11-1999 19-09-2000 30-01-2001 18-11-1999 04-02-1999 18-11-1999 10-05-2000 28-02-2001 28-10-2001 21-02-2001 21-01-2000 |

THIS PAGE BLANK (USPTO)